



# Potential effects of changes in climate and emissions on distribution and fate of perfluorooctane sulfonate in the Bohai Rim, China



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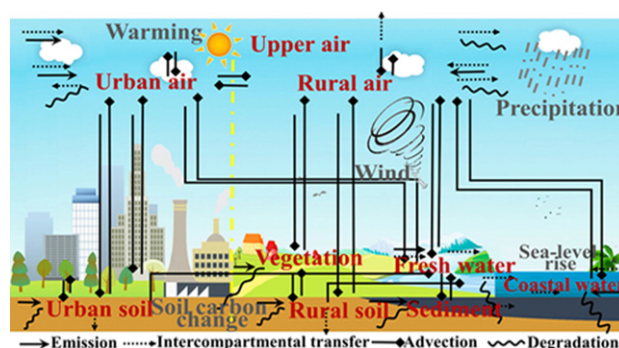
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## HIGHLIGHTS

- Climate change could have significant effects on fates of PFOS.
- Precipitation and temperature were the predominant affecting factors.
- A decrease in concentrations of PFOS is predicted for fresh water and urban soil.
- Predicted concentrations of PFOS in coastal water and rural soil will increase.
- Emission rates of POPs also played an important role in the fates of POPs.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 25 July 2017

Received in revised form 3 September 2017

Accepted 3 September 2017

Available online 14 September 2017

Editor: Jay Gan

### Keywords:

Multimedia model

Regional scale

Urbanization

Adaptation

Management

## ABSTRACT

Climate change and emissions rates of contaminants are expected to affect distribution and fate of Persistent Organic Pollutants (POPs) in the environment, however, studies on these combined factors are rare. In this study, Perfluorooctane Sulfonate (PFOS) is used as an example to assess how those two factors synthetically affect fate and disposition of POPs in the Bohai Rim of China by using the Berkeley-Trent-Urban-Rural (BETR-Urban-Rural) model. We set up three climate change scenarios and four emission scenarios to conduct the simulations. The results show that climate change could have significant effects on the transport and fate of PFOS mainly including advection, inter-compartmental transfer under the “worst case” emission scenario. For most grids, a remarkable decrease in concentrations of PFOS are predicted for fresh water and urban soil in the future, with precipitation and temperature being predominant factors, whilst for coastal water and rural soil, an increasing trend is predicted. Additionally, predicted sum of sources to the Bohai Sea increases greater than removals from the Bohai Sea in the future, adding evidence that concentrations of PFOS in coastal water will increase more in the future. Under scenarios of reduced emissions and climate change, concentrations of PFOS in each

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compartment decreased more rapidly over time. We suggest that assessment of future climate change impacts on fate of PFOS could take emission reductions into consideration.

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## 1. Introduction

Persistent organic pollutants (POPs) have properties of persistence, toxicity, potential bioaccumulation and long-range transport. Due to these properties, particularly the long-range transport which results in dispersed contamination far from sources, behaviors, fates, and exposures of POPs in the environment are a great concern for international environmental organizations, governments, academics and the public. Results of studies have shown that fates and behavior of POPs are affected by various factors, including chemical properties, environmental parameters like surface temperature, precipitation, wind speed, and soil solids organic carbon fractions, to name a few (Prevedouros et al., 2004a; Prevedouros et al., 2004b).

Human activities have been leading to global climate change, but also humans are responding and adapting to it (Clayton et al., 2015; Karl and Trenberth, 2003). Influences of climate change on the environment have been found in a wide range of aspects, such as terrestrial ecosystem, hydrological systems, coastal processes, freshwater ecosystems, and marine ecosystems (Hoegh-Guldberg and Bruno, 2010; Richardson and Schoeman, 2004; Rosenzweig et al., 2008; Scholze et al., 2006). Also, climate change could have far-reaching effects on POPs revolatilization and deposition by affecting environmental processes (Ma and Cao, 2010; Ma et al., 2011; Teran et al., 2012; Zhou and Ma, 2013). In general, mechanisms by which climate change can affect environmental behaviors and fates of POPs are of three basic types. First, these changes are likely to affect the environmental behavior of POPs by reinforcing the volatilization from primary and secondary sources (Ma et al., 2011). Second, they can influence the transport behavior of POPs by affecting their partitioning between compartments through processes such as air-surface exchange, rain dissolution, wet/dry deposition, and degradation rates indirectly (Teran et al., 2012). Third, they can affect rates of transformation, dilution, or decomposition of POPs, then ultimately change their concentrations and distributions in various compartments of the environment (Zhou and Ma, 2013).

However, understanding of these mechanisms is qualitative in most of the previous studies, and a more quantitative assessment of potential impacts is needed (Woehrschimmel et al., 2013). Recently, a few studies have explored these potential effects by use of models, with various scenarios of climate change. The results demonstrated that climate change could have significant influences on fate and concentrations of POPs like PAHs, PCBs with temperature, precipitation, and wind speed being predominant factors while varying from pollutants and environmental media (Cai et al., 2014; Gouin et al., 2013; Lamon et al., 2009; Ma and Cao, 2010; Paul et al., 2012; Song et al., 2016a). However, there have been few studies that explore not only the net effects of climate change but also the integrated impacts combining the climate change and emission reduction policies.

PFOS, as one of the most abundant old-generation members of PFAS family, is an emerging POP, and is one of the pollutants that are most persistent in the environment. PFOS and related substances are synthetic chemicals, manufactured for their desirable features of chemical stability, high surface activity, water and oil repellence (Giesy and Kannan, 2001, 2002). In 2004, China began to produce PFOS-based products on a large scale, and annual production of PFOS-related chemicals grew rapidly from 2003 to 2011 (Xie et al., 2013a). PFOS has been detected in various compartments in China recently (Liu et al., 2016; Su et al., 2016; Su et al., 2017b; Wang et al., 2014).

The objective of this study is using the Berkeley-Trent-Urban-Rural model (Song et al., 2016b) to explore how changes in emission rates

and climate including temperature, precipitation, wind speed, soil carbon stock, and sea-level rise would affect the concentrations of perfluorooctane sulfonate (PFOS) in the Bohai Rim of China, as well as differences between urban and rural areas. We also aim at identifying the key factors affecting concentrations of PFOS under the climate change scenarios (Special Report on Emission Scenarios (SRES) B1, A1B, and A2 in IPCC, 2007), as well as the mass fluxes of PFOS to the Bohai Sea. Also, since PFOS is being phased out, it will provide an opportunity to validate the results of the model with changing rates of release. The results of this model will allow predictions for other POPs with PFOS-like properties, and this model can be applied to predict the influences of climate change on transport behaviors of other POPs. The outcome of this research would be useful for planning PFOS emission reduction and ecosystem protection.

## 2. Methods

### 2.1. Model description and study area

The original Berkeley-Trent (BETR) model is based on fugacity approach, whereby a joint system of seven discrete and homogeneous compartments is regarded as one segmentation (or grid) (Mackay, 2001; MacLeod et al., 2001). It includes four basic processes of POPs behavior: emissions to environment, advection, inter-compartmental transport, and degradation. The BETR model has been successfully used to simulate relative and absolute fates of chemicals in various environments in North America (MacLeod et al., 2001; Woodfine et al., 2001), Europe (Prevedouros et al., 2004a; Prevedouros et al., 2004b), and the global environment (MacLeod et al., 2005).

We take account for effects of urbanization, and improve the BETR model, called BETR-Urban-Rural, which divides the soil compartment into urban soil and rural soil, lower air compartment into lower urban air and lower rural air based on the land-use information (Song et al., 2016b). The urban areas contain industrial land, built-up land, commercial districts, urban residential areas, municipal land for public facilities, and their buffers. Except for urban areas, in this model rural areas are defined as a combination of rural villages, rural residential areas, agricultural land, forest land, grassland, unused land and so on (Wang et al., 2010). In the BETR-Urban-Rural model, the environment within each grid contains nine compartments. Specific environmental parameters for an urban area like perimeter of urban area, urban-rural atmospheric mixing rate, freshwater coverage rate of urban area etc. and transfer processes between urban and rural areas were also improved. More information about the model can be found in Song et al. (2016b). In this study, the BETR-Urban-Rural model is used to make projections under three scenarios for climate change (B1, A1B, and A2) in Intergovernmental Panel on Climate Change (IPCC), 2007 and four scenarios for emissions over three 20-year periods throughout the 21st century (2016–2035, 2046–2065, and 2081–2100), relative to the baseline simulation on steady state for 2010.

The Bohai Rim, including parts of the Bohai Sea and the area around it, is one of the most developed regions in China. The study area covers Beijing city, Tianjin city, parts of Liaoning, Hebei and Shandong provinces. A great number of industries are located in this region, including metal plating, textile treatment, production of firefighting chemicals and semiconductor industries, some of which are relevant to industrial sources of PFOS and related substances (Xie et al., 2013b). Rapid urbanization and industrial development have caused a significant growth in production and energy consumptions and releases of pollutants, leading

to further and multiple environmental problems, such as metal or organic chemical pollution (Su et al., 2017a; Wang et al., 2014; Xu et al., 2013).

The longitude of Bohai Rim is from 116°E to 124°E, while latitude is from 36°N to 43°N. The study area is split into 56 grids by  $1^\circ \times 1^\circ$  (Fig. 1). The land use information of study area can also be seen in Fig. 1. For the study area, each grid contained 9 compartments which are upper air, lower rural air, lower urban air, vegetation, rural soil, urban soil, fresh water, fresh water sediment, and coastal water. Parameterization about the BETR model (and BETR-Urban-Rural model) in the Bohai Rim has been published by Liu et al. (2014), Liu et al. (2015) and Song et al. (2016b). The effects of long-range transport of upper air could be ignored because the value of that was thought to be limited within this region (Liu et al., 2014; Liu et al., 2015; Song et al., 2016b). The 56 sub-grids are connected by air, fresh water and coastal water advection between neighboring grids, and the runoff of fresh water to coastal water was also considered.

## 2.2. Physical-chemical properties of PFOS

The physical-chemical properties of PFOS considered in the BETR-Urban-Rural model are listed in Table S1 (3M, 2003; Ahrens et al., 2011; Arp et al., 2006; Brooke et al., 2004; Chen et al., 2012; Löfstedt Gilljam et al., 2015; OECD, 2002).

## 2.3. Emission scenarios

According to the emission estimation methodology developed by our research group, emissions of PFOS and its related substances (including PFOS, FOSAs, FOSEs, POSF) to each compartment were estimated in China for 2010 (Xie et al., 2013a; Xie et al., 2013b). Spatially distributed emissions were estimated for the study area in 2010 depending on the location of industrial plants, as well as the domestic emissions related to population density, and per capita disposable income (Liu et al., 2015; Xie et al., 2013a; Xie et al., 2013b). In this study, it was assumed that all PFOS-substances degraded to PFOS immediately, and the formation factor was 0.94, since the previous research results showed that the quantity of PFOS-salts came from degradation of PFOS substances was rather smaller than that from direct emissions (Liu et al., 2015).

Four different future emission scenarios were proposed for the three 20-year periods to the year 2100. Emission scenario 1 is a “worst case” scenario, under the assumption that current annual emissions of PFOS keep continuing. Since PFOS and its related substances were listed in the Stockholm Convention on POPs in 2009, in China, production of PFOS-related chemicals fluctuated and then stabilized at approximately 250 t/yr (Xie et al., 2013b). So continued emission of PFOS until 2100 was assumed to be the same as it was in 2010. This is also a reference scenario (keeping emission constant) in order to explore the effects of future climate change under the hypothesis that there are no any control policies and management on PFOS.

Emission scenarios 2, 3, and 4 are based on the contingency that China, in compliance with the international treaties and national regulations, will begin to phase out PFOS and similar chemicals, then use alternatives fully by 2030, 2050, or 2100, respectively. It is assumed that the production and usage of PFOS will decrease linearly from 2017 to zero in the final year. Under this assumption, we calculate the emissions of PFOS in specific periods (Table S2). Since 2014 when the Chinese government has set a series of regulations on production and use of PFOS to comply with the Stockholm Convention, it has been encouraging development of alternatives. However, the regulations did not yet set the final year for withdrawal. Therefore, three scenarios are selected to give a range of possibilities. In the year when the final manufacture of PFOS is stopped, releases will not be suddenly stopped because of applications by secondary users (like metal plating, fire-fighting, semiconductor, domestic users and so on). For all secondary users, a worst-case situation is foreseen in which stock for each application is enough during its shelf life and after which all expired products will not be used. Hence, emissions from storage of secondary products would continue being released during the shelf-life period. Taking the use of aqueous fire-fighting foams as an example, shelf-lives of products are approximately 5 year, during which releases from the usage of stock products were assumed to be the same as that in the previous year of withdrawal. There are some differences between domestic users and industrial sectors for projected future emissions. For domestic applications, releases are assumed to decrease linearly as products come to the end of their natural life. For example, carpets are in use for an average of about 10 years, releasing one tenth of their treatment each year until eventual disposal (Paul et al., 2008). Finally, simulations for the three 20-year periods were made by use of annual mean emissions during each period. The

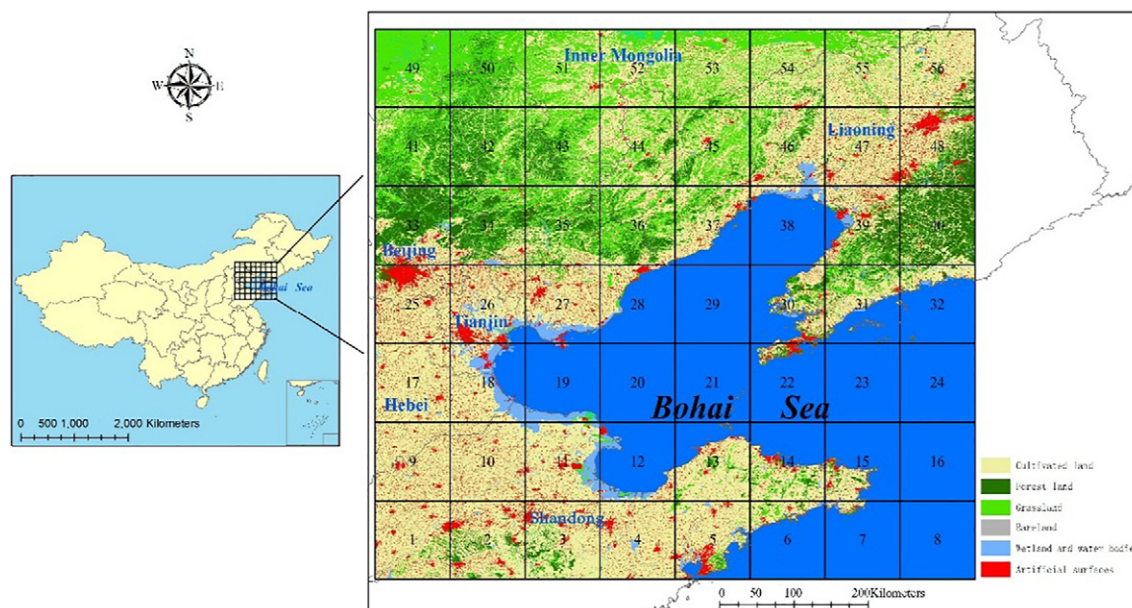


Fig. 1. Study area and definition of grid system used in the model.

estimated emissions of PFOS and their compartmental distribution in the study area under four emission scenarios are in Table S2.

#### 2.4. Brief introduction to climate change and urbanization scenarios

The changes of the following variables are considered for each climate change scenario (SRES B1, A1B, and A2 in IPCC, 2007): precipitation, temperature, sea-level rise, soil carbon stock, and wind speed, since these variables are important environmental parameters to run the model. The specific increase rates of these variables are presented in Table S3. The SRES scenarios explore alternative development ways, covering a series of emissions of greenhouse gases driving by demographic structure, economy and technology (IPCC, 2007). Scenarios B1, A1B, and A2 assume a convergent world, a rapid economic development world, and a world with rapid growth of population while slow economic growth and technological changes (IPCC, 2007). More information about SRES and scenarios B1, A1B, and A2 can be found in the IPCC Climate Change 2007 Synthesis Report.

##### 2.4.1. Precipitation

Precipitation and fresh water runoff were the most sensitive parameters (Liu et al., 2015). Precipitation could affect the transfer rates from air to other compartments. Gridded 10-year averaged precipitation rates in the study area were extracted for the periods 2016–2035, 2046–2065, and 2081–2100 (short of 2035, 2065, and 2100, the following, also called early, mid, and late 21st century respectively), which vary from grids and scenarios (Zhang et al., 2012). Overall, the annual mean precipitation anomaly was projected to increase over the study area by 3%–9% ( $10 \text{ yr}^{-1}$ ), 7.5%–18% ( $10 \text{ yr}^{-1}$ ), and 9%–18% ( $10 \text{ yr}^{-1}$ ) respectively, under all three scenarios for the three periods (Zhang et al., 2012).

##### 2.4.2. Temperature

Temperature could affect wet deposition, and densities of compartments, fugacity capacities of compartments in the fugacity approach. The same process was repeated for surface air temperature as precipitation, also varying from grids and scenarios (Zhang et al., 2012). Overall, the warming rate was projected to increase over the study area by 0.2–0.6 °C ( $10 \text{ yr}^{-1}$ ), 0.3–0.6 °C ( $10 \text{ yr}^{-1}$ ), and 0.1–0.6 °C ( $10 \text{ yr}^{-1}$ ) respectively, under all three scenarios for the three periods. Additionally, urbanization has an important influence on surface air temperature (Dirmeyer et al., 2010). The temperatures in urban areas often exceed those in the surrounding areas by several °C, a phenomenon termed “urban heat island effect” (Schulze and Langenberg, 2014). Hence, this effect was taken into account in the BETR-Urban-Rural model, and it was assumed to be 2.2 °C for that difference between urban areas and rural areas in the study area (Cao et al., 2016).

##### 2.4.3. Sea-level rise

Sea-level rise could impact the depth and volume of coastal water, and then impact the concentrations of PFOS in coastal water. The mean rate of rise in sea-level along the coast of China between 1980 and 2014 was 3.0 mm  $\text{yr}^{-1}$ . It was inferred that the sea-level of the Bohai Sea in the early 21st century was 0.045 m greater than that in 2010 for all three scenarios (Communique, 2014). The sea-level rise in mid and late 21st century was referred to the global mean data in IPCC AR4, being 0.26, 0.25, 0.30 and 0.28, 0.35, 0.37 m greater under the three scenarios, respectively (IPCC, 2007).

##### 2.4.4. Soil carbon stock

Organic carbon fraction in soil could have important influences on partitioning coefficient  $K_{\text{sw}}$  (soil solid – water). According to Peng et al. (2009) who predicted the changes of soil carbon stock under climate change scenarios, we set the average soil carbon stock with an increase by 5% for the 2030s, 4% for the 2060s and by 3% for the 2090s, respectively, under the three climate change scenarios B1, A1B and A2 (Peng

et al., 2009). Additionally, soil carbon stock was approximately 57.76% less in urban land than that in non-construction land (forest land and green open spaces) in China (Tao et al., 2015).

##### 2.4.5. Changes in velocities of wind

Wind velocities could change the air flux matrix, and then influence the transport of PFOS by air advection. A study predicted that the annual mean wind speeds in China for the 21st century by many climate models, which suggested that they varied slightly under all three scenarios (Jiang et al., 2010). From the whole study area, under all three climate change scenarios and periods, the increasing rates of mean winds varied from –0.1 to 0.1 m/s (Jiang et al., 2010).

Additionally, projection of rainfall-runoff relationship was developed in the model which was referred to a regression model fitting the relationship between runoff and precipitation (Chen and Wang, 2004). Also, rapid urbanization is one of the outstanding features in China, particularly in coastal regions. Covering proportion by urban land in grids is an important parameter in the BETR-Urban-Rural model. Based on the estimation of World Urbanization Prospects 2011, the urbanization rates of China would increase by 30.48%, 58.45%, 70.49% to the early, mid, and late 21st century relative to the 2010, respectively (Desa, 2011).

### 3. Model output and validation

Inputting corresponding emission data and environmental parameters, the model is run 18 times to steady state solutions, under each climate change scenario for each emission scenario. Results of previous research showed that coastal water, soil, fresh water, and sediment were the four primary sinks for PFOS, and that storage in air and vegetation was less than 1.00% (Liu et al., 2015). Consequently, concentrations and transport processes of PFOS in coastal water, urban soil, rural soil, fresh water, and sediment were the primary compartments analyzed in this study. Median values of modeled concentrations of PFOS in fresh water, sediment, urban soil, and rural soil during 2010 were 7.68 ng/L, 0.40, 0.60, and 0.026 ng/g dw, respectively.

Additionally, accuracy of simulations was assessed by comparing simulated baseline concentrations of PFOS with measured data in fresh water, fresh water sediment, urban soil, and rural soil in the study area (Table S4). Available measured concentrations of PFOS from 2009 to 2011 were collected from published sources. Comparing with the ranges of the two datasets, the range of simulated concentrations was generally consistent with measured concentrations of PFOS for all compartments (Table S4). In most cases, the minimal value of the modeled concentrations was a little higher than that of the measured concentrations, while the maximal modeled value was a little lower than the measured one. These differences would be attributed to the temporal and spatial variability of measured concentrations of PFOS, while the modeled concentrations represent the annual mean values for grids (Wang et al., 2016). The estimated releases are not exactly the same as the actual ones, and the values of some parameters are default or empirical values, which may cause deviations of model results.

#### 3.1. Spatially projected changes in concentrations of PFOS

##### 3.1.1. Emission scenario 1

Changes in concentrations of PFOS in fresh water, coastal water, urban soil, and rural soil under three future climate change scenarios and four emission scenarios are given (Table S5). Ratios of projected period concentration and baseline concentration are used to describe changes in concentrations of PFOS. It shows that there is a similar changing trend for those four compartments among the three climate change scenarios B1, A1B and A2 under each specific emission scenario (Table S5). Fig. 2 shows the projected changes in concentrations of PFOS in those four compartments for emission scenario 1, taking specific

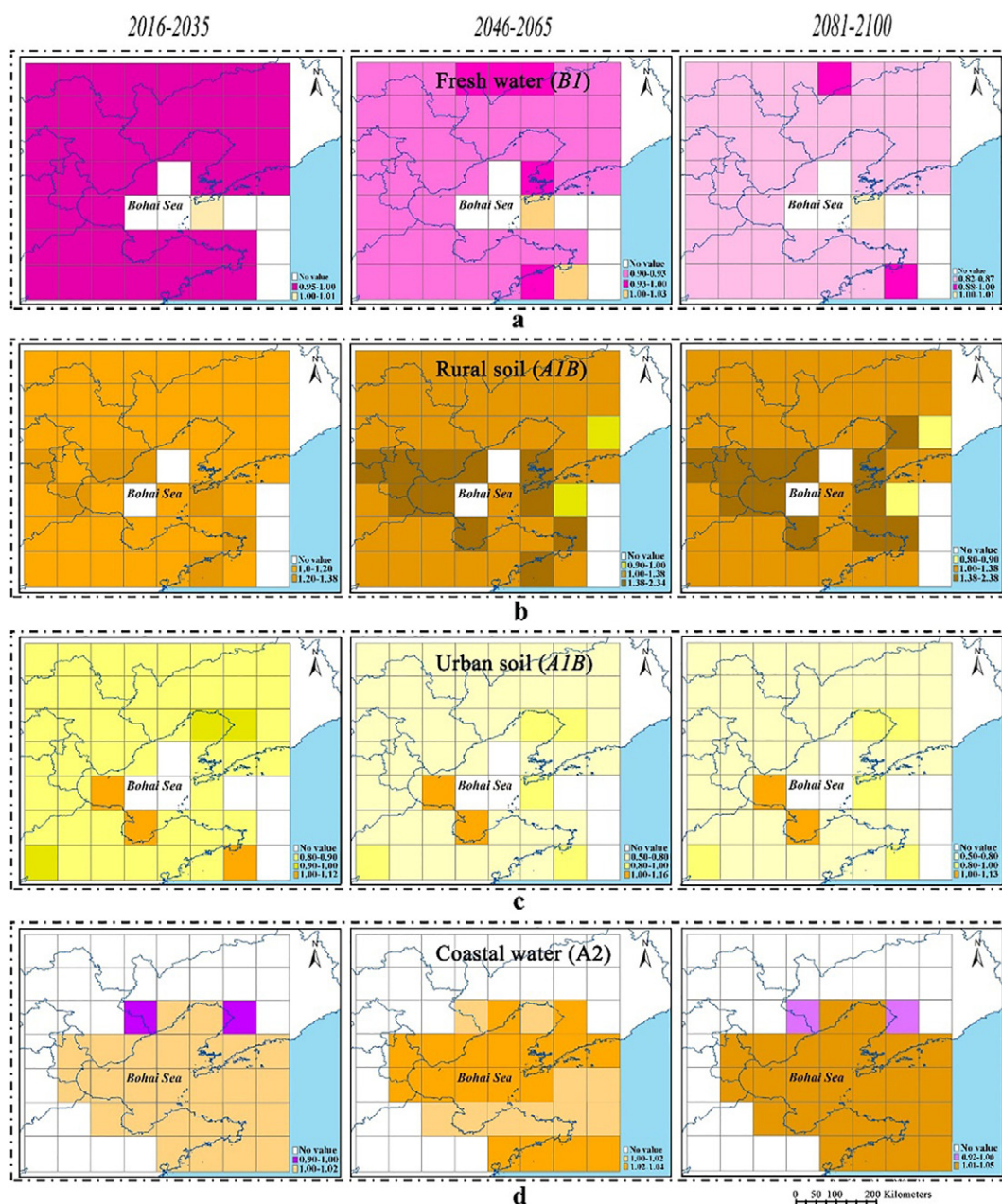


Fig. 2. Projected changes in concentrations of PFOS in fresh water, rural soil, urban soil and coastal water under specific climate change scenario for emission scenario 1.

climate change scenario as an example for each compartment. Large decreases in concentrations of PFOS during simulations of future conditions are observed in fresh water, as well as for urban soil (except for some grids) (Fig. 2). Taking grid 26 (Haihe River in Tianjin City, seen in Fig. 1) as an example, ratios of concentration in the early, mid, and late 21st century for fresh water were 0.9616, 0.9294, 0.8472, and for urban soil were 0.8708, 0.7530, 0.7300 under climate change scenario B1. Under scenarios A1B and A2, fresh water concentration ratios were 0.9414, 0.8849, 0.8329 and 0.9750, 0.9220, 0.8318 in the future three periods, while concentration ratios for urban soil were 0.8698, 0.7515, 0.7286 and 0.8693, 0.7504, 0.7218 during the three future periods, respectively.

PFOS in fresh water and urban soil are predicted to exhibit rapid decline. The key reason for the decline of PFOS in fresh water is the dramatic increment of freshwater runoff associated with increasing precipitation even though it brings the PFOS in air, soil to aquatic ecosystems through wet deposition, rain dissolution and surface runoff from land to water with the increasing precipitation. According to the

regression relationship between runoff and precipitation (Chen and Wang, 2004), runoff is predicted to have an increase, particularly for the mid and late 21st century, with increases under scenario B1 of 5.59%, 10.54%, 19.15% in the three future periods, respectively. Alternatively, warming water would reduce the fugacity capacity of PFOS in fresh water. This is similar with the research results of Europe, where precipitation and temperature were the predominant factors to influence the fate and transport of PCB 153 (Paul et al., 2012). For urban soil, the major reason for PFOS concentration reduction was that emission was constant under the emission scenario 1 while with greater urbanization and extended urban land. And the extended urban land would increase the transport fluxes from urban soil to fresh water due to runoff scouring. Additionally, the increasing transpiration stream concentration factor (TSCF) driven by temperature would make the transport flux from urban soil to vegetation rise. Therefore, it is possible that concentrations of PFOS will decrease in urban soil in the future.

On the contrary, for most grids, concentrations of PFOS in rural soil and coastal water exhibited opposite trends. For example, under

scenario A1B, in grid 26 (Tianjin City), in rural soil, concentration ratios were 1.1705, 1.3855, 1.4618 in the future three periods, while under scenario A2, ratios for coastal water were 1.0029, 1.0188, 1.0359 in the future three periods, respectively. For rural soil, under the “worst case” emission assumption while the population and land-use areas decrease along with urbanization process, it is reasonable to simulate greater concentrations in the future. For coastal water, runoff from fresh water to coastal water increased greatly owing to higher precipitation in the future. This would affect accumulation of PFOS in coastal water. This prediction is consistent with coastal water acting as a sink for PFOS (Liu et al., 2015).

### 3.1.2. Projected changes in concentrations of PFOS under scenarios where emissions are reduced

Table S5 shows projected changes in concentrations of PFOS in fresh water, rural soil, urban soil and coastal water under each climate change scenario for reduced emission scenarios 2, 3 and 4, since PFOS was listed in Stockholm Convention in 2009. For emission scenario 2, the concentrations of PFOS in fresh water in the whole area will decrease by 60% or more during the early 21st century. For rural soil, urban soil and coastal water, concentrations of PFOS also will decrease in the early 21st century (Table S5).

For emission scenarios 3 and 4, except for a few grids, concentrations of PFOS in the four compartments are predicted to have a large reduction as a result of decreasing emissions and climate change over time. Particularly for emission scenario 4, with the assumption of PFOS withdrawn in the late 21st century, concentrations of PFOS are predicted to decrease by about 90-fold in the later part of the 21st century. In this regard, under the combined influences of emission and climate change,

there are big decreases in transfer fluxes between compartments. Taking grid 26 as an example, under emission scenario 2 and climate change scenario B1, the transfer fluxes between compartments are predicted to decrease by 54%–70% in the early 21st century, which is similar to the decreases of emission rates.

In a word, with constant emission rate, climate change affects the distribution and fate of PFOS primarily by changing the advection via water, and transport rates between compartments, while transport fluxes would decrease along with the decline of emission rates.

### 3.2. Changes in annual mass fluxes of PFOS to the Bohai Sea

In order to explore effects of climate change on fluxes of PFOS to the Bohai Sea, changes in total annual mass flux are discussed under emission scenario 1 and climate change scenario A1B because it is a moderate choice. Total annual mass fluxes of PFOS to the Bohai Sea for baseline 2010, and the ratios of the fluxes for the years 2035/2010, 2065/2010 and 2100/2010 are presented in Fig. 3.

For pathways of PFOS to the Bohai Sea, rain dissolution, wet deposition, and fresh water runoff will all increase during the three future periods, relative to the baseline of 2010. Rain dissolution will increase by 1.90%, 7.55%, 15.70%, wet deposition will increase in ascending order by 1.45%, 7.40%, 13.03%, while fresh water runoff will increase by 1.11%, 9.11%, 18.31% in 2035, 2065, and 2100, respectively, relative to 2010. These changes are owing to projected increased precipitation in the future. Air diffusion and dry deposition are predicted to first increase slightly in 2035, then decrease in 2065 and 2100, but the inputs remain more than losses through outflow and degradation. For removal pathways, outflow and degradation fluxes will both increase further in the

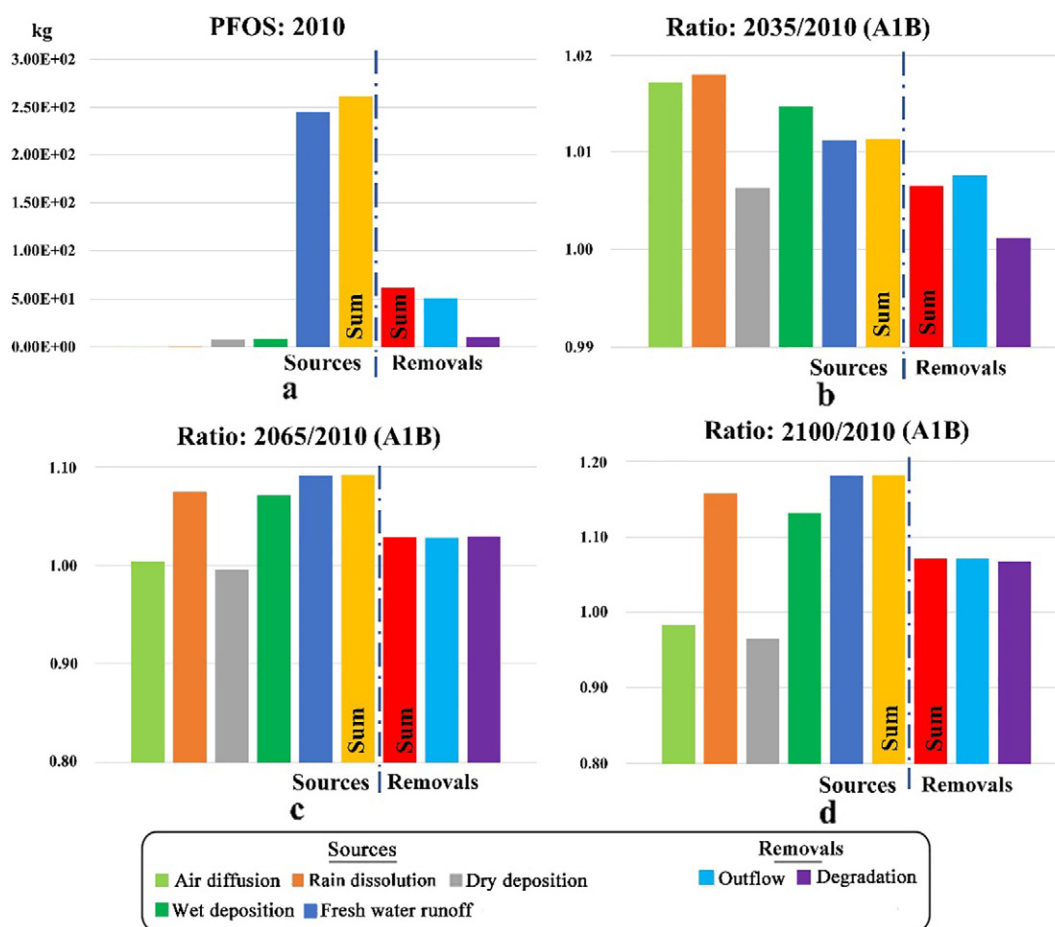


Fig. 3. Total annual mass fluxes (kg) to the Bohai Sea, sources and removals for (a) 2010. Ratios of total annual mass fluxes: (b) 2035/2010, (c) 2065/2010, and (d) 2100/2010 under scenario A1B.

future, relative to 2010. The sum of sources will increase by 1.12%, 9.11%, 18.31%, and that of removals by 0.66%, 2.77%, 7.14% in 2035, 2065, and 2100, respectively. The sum of the sources (the left of the dotted line) is always greater than the sum of the removals (the right of the dotted line), and differences between them are projected to be larger in the future. This is in addition to evidence that concentrations of PFOS in coastal water will increase more in the future. This prediction is inconsistent with the modeled results for loading of  $\gamma$ -HCH and PCB 153 to the North Sea (O'Driscoll et al., 2014), because these chemicals have distinct physical–chemical properties. So the general result is that there are large influences of climate change on the mass fluxes of PFOS to the Bohai Sea.

### 3.3. Changes in fate and transport of PFOS: case study of Tianjin city

In this section, grid 26 (containing the vast majority of Tianjin City) is used as an example to analyze effects of future climate changes

(scenario A1B) on fates and transportation of PFOS in more detail, including advection fluxes between adjacent grid (inflow/outflow fluxes of air), degradation, and intermedia transportation (Fig. 4). Under emission scenario 1, due to the increasing mean wind speed, both inflow and outflow fluxes will increase, particularly in the mid and late 21st century, by 5.91%, 8.21% for inflow flux, and 3.87%, 5.38% for outflow flux. Temperature independent degradation will decrease slightly over time since rates of degradation are complex and related to volume of each environmental compartment, concentrations of PFOS in each compartment, and first-order reaction rate constant (Mackay, 2001; MacLeod et al., 2001). The values in Fig. 4 (b)–(e) are the sum of all environmental compartments, hence, its reduction was closely linked with the decrease of concentrations of PFOS in fresh water, sediment, urban soil, rural soil, and rural air.

For intermedia transport processes, movements from fresh water to coastal water, fresh water to sediment, and sediment to fresh water are

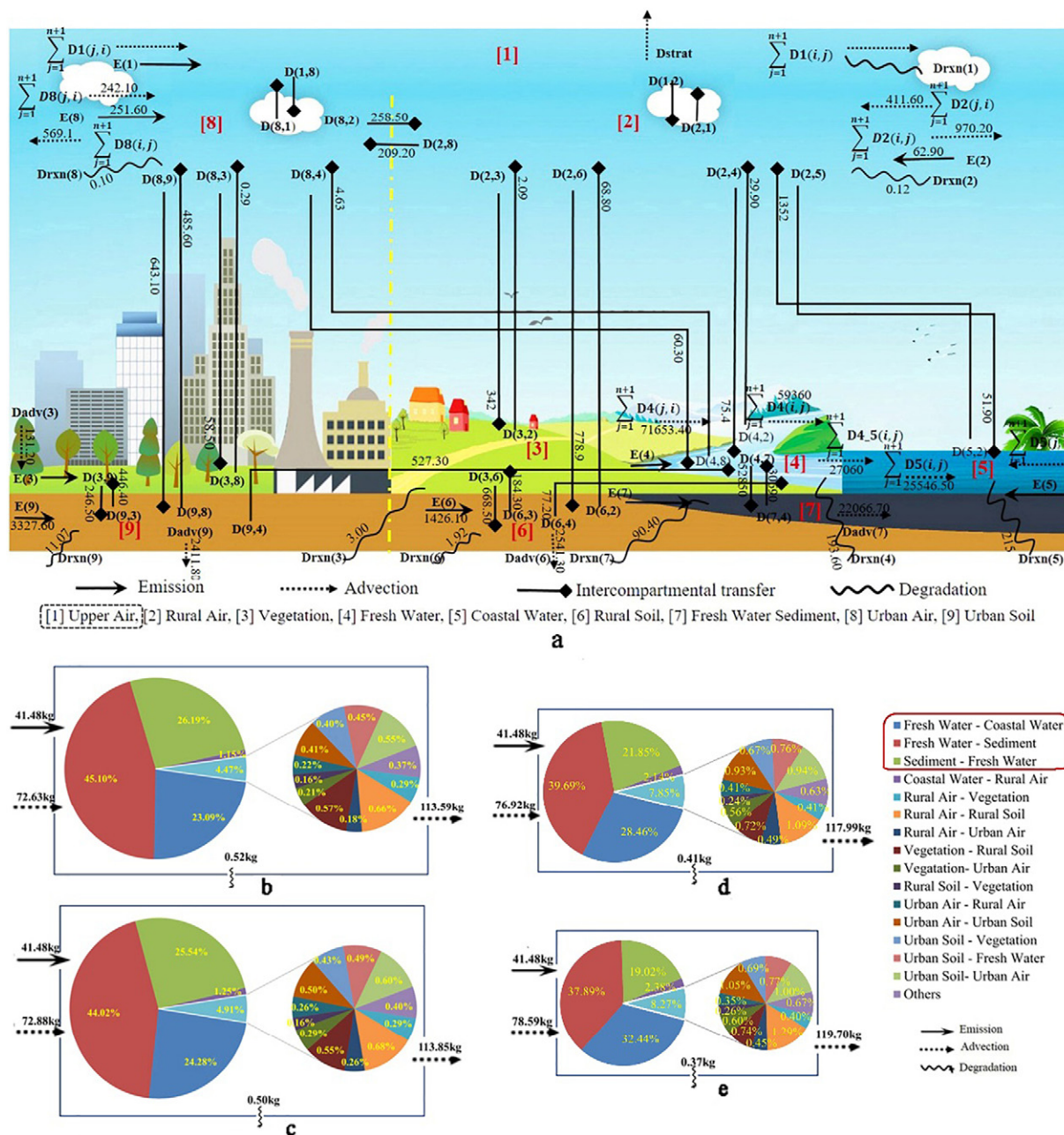


Fig. 4. (a) Model structure and transfer flux of PFOS for each process in grid 26 during 2010 (g/yr); and a summary of mass balance of PFOS for grid 26 (b) baseline 2010, (c) 2016–2035, (d) 2046–2065, (e) 2081–2100 under emission scenario 1, moderate climate change scenario A1B. Note: the size of the pies indicates the total amount of intermedia transport flux.

the three predominant transfer pathways among all transfer processes (Fig. 4). Among these three pathways, transfer rate from fresh water to coastal water increases rapidly over time, from 1/4 of the total in 2010 to 1/3 of the total in the late 21st century. It is due to increased runoff from fresh water to coastal water as a result of increased precipitation in the mid and late 21st century. Rates of transfer along the other two predominant pathways will be less in the future, especially in the mid and late 21st century (Fig. 4 (d)–(e)). Due to transfer between fresh water and sediment, along with decreases in concentrations in fresh water, concentrations of PFOS in sediment will also decrease, as well as the transfer rate between them.

#### 4. Conclusion

In this study, PFOS was used as an example to assess how future changes in climate and emissions of contaminants synthetically affect concentrations and disposition of POPs. The BETR-Urban-Rural model was further developed to explore the potential integrative effects, taking effects of urbanization into consideration at the same time. Results of simulations suggested that emission rate, degradation rate, and intermedia transfer processes would affect concentrations and disposition of PFOS. Under the influences of climate change (including temperature, precipitation, sea-level rise, wind speed, and soil carbon stock) and urbanization, the projected concentrations of PFOS in compartments fresh water and urban soil would decrease much in the future, potentially lowering the exposure burden to biota in fresh water and urban soil, as a result of increased temperature, precipitation, and urbanization. While coastal water and rural soil displayed an opposite trend, which would bring about more adverse effects and risks to organisms, particularly for the marine ecosystem. Besides, potentially large influences in changes of climate on mass fluxes of PFOS to the Bohai Sea were identified. It is important to point out that these projected changes would occur under the “worst case” scenario and climate change scenarios referred to IPCC, 2007. Since the Paris Agreement entered into force in 2016 (Climate Change Secretariat, 2016), future climate change would be mitigated as well as the effects on POPs fate. Outcomes from other emission scenarios showed that through modern, effective chemical management practices and legislation, chemicals with PFOS-like properties might be effectively regulated and reduced. This points to the necessity of including climate change mitigation and adaptation, as well as urbanization planning in the future policy-making of emission reduction.

#### Acknowledgements

This study was supported by the National Key R & D Program of China (2017YFC0505704), and the National Natural Science Foundations of China under Grant No. 414201040045 and No. 41371488.

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2017.09.021>.

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